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# Comment on “A spherical cavity model for quadrupolar dielectrics” [J. Chem. Phys. **144**, 114502 (2016)]

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Recently, a spherical cavity (Onsager) model for quadrupolar dielectrics has been proposed and used to calculate the macroscopic quadrupolarizabilities of several common solvents.<sup>1</sup> In this Comment, one of the boundary conditions used in Ref. 1 (for continuity of the displacement field) is revised to account for the surface displacement field that occurs at non-homogeneously polarized interfaces. We show that the revised condition leads to more reasonable results.

The displacement field  $\mathbf{D}$  in a quadrupolar medium involves the divergence of the quadrupolarization tensor  $\mathbf{Q}$ ,

$$\mathbf{D} = \varepsilon \mathbf{E} - \frac{1}{2} \nabla \cdot \mathbf{Q}, \quad (1)$$

where  $\varepsilon$  is the dielectric permittivity and  $\mathbf{E}$  is the electric field intensity. In order to solve Coulomb's equation ( $\nabla \cdot \mathbf{D} = 0$ ) for problems involving an interface between two quadrupolar media, a boundary condition is required for  $\mathbf{D}$ . In Ref. 1, we used the condition for continuity of the normal displacement field ( $D_r$ ) at the surface of the spherical cavity, Eq.<sup>1</sup> (8) (we cite the equations from Ref. 1 with superscript 1),

$$D_r(r = R_{\text{cav}} - 0) = D_r(r = R_{\text{cav}} + 0), \quad (2)$$

where  $R_{\text{cav}}$  is the radius of the cavity. This condition is valid only in case that  $\mathbf{D}$  has no  $\delta$ -term in its singular expansion at the surface of discontinuity (i.e., if  $\mathbf{D}$  can be expressed as  $\mathbf{D}^+ \eta^+ - \mathbf{D}^- \eta^-$ , where  $\eta^+ = \eta(r - R_{\text{cav}})$  and  $\eta^- = \eta(R_{\text{cav}} - r)$ , and  $\mathbf{D}^+$  and  $\mathbf{D}^-$  are continuous functions of the coordinates in the vicinity of  $r = R_{\text{cav}}$ ;  $\eta$  and  $\delta$  are the Heaviside and Dirac functions). However, the quadrupolarization tensor is discontinuous at the interface between the cavity and the medium, i.e.,  $\mathbf{Q} = \mathbf{Q}^+ \eta^+ + \mathbf{Q}^- \eta^-$ ; from Eq. (1), it then follows that  $\mathbf{D}$  does have a  $\delta$ -term,

$$\mathbf{D} = \mathbf{D}^+ \eta^+ + \mathbf{D}^- \eta^- + \mathbf{D}^S \delta, \quad (3)$$

where the bulk displacements  $\mathbf{D}^\pm$  stand for

$$\mathbf{D}^\pm = \varepsilon^\pm \mathbf{E}^\pm - \frac{1}{2} \nabla \cdot \mathbf{Q}^\pm, \quad (4)$$

and the surface displacement field  $\mathbf{D}^S$  is given by

$$\mathbf{D}^S = -\frac{1}{2} \mathbf{e}_r \cdot (\mathbf{Q}^+ - \mathbf{Q}^-). \quad (5)$$

Here,  $\delta \equiv \delta(r - R_{\text{cav}})$ ,  $\mathbf{e}_r$  is the unit vector normal to the surface, and we used the relations  $\nabla \eta^\pm = \pm \mathbf{e}_r \delta$ . The correct boundary condition in the case of non-zero  $\mathbf{D}^S$  reads<sup>2–4</sup>

$$D_r(r = R_{\text{cav}} - 0) = D_r(r = R_{\text{cav}} + 0) + \nabla^S \cdot \mathbf{D}^S \Big|_{r=R_{\text{cav}}}, \quad (6)$$

where  $\nabla^S$  is the surface nabla operator ( $\nabla^S = \nabla - \mathbf{e}_r \partial / \partial r$ ). The derivations of this equation in Refs. 3 and 4 were for a flat surface, and  $\mathbf{D}^S$  in Ref. 4 is produced by intrinsic surface polarization. Nevertheless, Eq. (6) is valid<sup>2</sup> also for the case we investigate—spherical surface and  $\mathbf{D}^S$  induced by the discontinuity of the bulk quadrupolarization, Eq. (5) (cf. the supplementary material). The term  $\nabla^S \cdot \mathbf{D}^S$  is zero for the problems of quadrupolar electrostatics we solved previously,<sup>5–7</sup> since the involved surfaces were homogeneous. However, this is not the case with the four basic problems required by the Onsager model of quadrupolar dielectrics solved in Ref. 1. The revised expressions follow.

**Reaction fields of a dipole and a quadrupole.** With regard to the problem for a dipole  $\mathbf{p}$  in the centre of a cavity, the solution for the potential  $\phi_{p0}$  inside the cavity ( $r < R_{\text{cav}}$ ) remains formally the same (Eq.<sup>1</sup> (13)), but the one outside the cavity is, instead of Eq.<sup>1</sup> (14),

$$\phi_p = \frac{\mathbf{p}_{\text{ext}} \cdot \mathbf{r}}{4\pi \varepsilon r^3} \left( 1 - \frac{9}{g_p} \frac{L_Q^2}{R_{\text{cav}}^2} \frac{r + L_Q}{R_{\text{cav}}} e^{-\frac{r - R_{\text{cav}}}{L_Q}} \right). \quad (7)$$

Here  $L_Q$  is the quadrupolar length. The external dipole moment  $\mathbf{p}_{\text{ext}}$  in Eq. (7) is proportional to  $\mathbf{p}$ ,

$$\mathbf{p}_{\text{ext}} = Y_E \mathbf{p}, \quad (8)$$

where  $Y_E$  is given by Eq.<sup>1</sup> (28),  $Y_E = 3f_E \varepsilon / (2\varepsilon + f_p \varepsilon_0)$ . The quadrupolar factors  $f_p$ ,  $g_p$ , and  $f_E$  in the formulae above stand for the expressions

$$f_p = \frac{2 + 8x}{2g_p + 9x^2 + 9x^3}, \quad f_E = \frac{2g_p}{2g_p + 9x^2 + 9x^3}, \quad (9)$$

$$g_p = 1 + 4x + 9x^2 + 9x^3,$$

where  $x = L_Q / R_{\text{cav}}$ ; the formula Eq.<sup>1</sup> (17) for  $f_p$  is invalid. The expression Eq.<sup>1</sup> (15) for the reaction field  $\mathbf{E}_{\text{react}}$  remains formally unchanged but with the new factor  $f_p$ . The calculated limit in Eq.<sup>1</sup> (18) holds true with the new formulae presented here; note that it is actually incorrect with the old ones due

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to an arithmetic mistake. This means that the revised Onsager model following from the new boundary condition (6) leads to the correct continuum single particle limit of the perturbation theory of Milischuk and Matyushov,<sup>8</sup> while the old one<sup>1</sup> stemming from Eq. (2) does not.

Similar corrections are required in the formulae<sup>1</sup> (20)–(24) for the reaction field of a quadrupole  $\mathbf{q}$  in a cavity. Instead by Eq.<sup>1</sup> (21), the potential  $\phi_q$  at  $r > R_{\text{cav}}$  is given by

$$\phi_q = \frac{3\mathbf{r} \cdot \mathbf{q}_{\text{ext}} \cdot \mathbf{r}}{8\pi\epsilon r^5} \left( 1 - \frac{18}{g_q} \frac{L_Q^2}{R_{\text{cav}}^2} \frac{r^2 + 3L_Q r + 3L_Q^2}{R_{\text{cav}}^2} e^{-\frac{r-R_{\text{cav}}}{L_Q}} \right). \quad (10)$$

The external quadrupole moment  $\mathbf{q}_{\text{ext}}$  is still proportional to  $\mathbf{q}$ , but instead of Eq.<sup>1</sup> (23), the relation is

$$\mathbf{q}_{\text{ext}} = Y_{\nabla E} \mathbf{q}, \quad (11)$$

where  $Y_{\nabla E}$  is given by Eq.<sup>1</sup> (33), i.e.,  $Y_{\nabla E} = 5f_{\nabla E}\epsilon/(3\epsilon + 2f_q\epsilon_0)$ . The quadrupolar factors  $f_q$ ,  $f_{\nabla E}$ , and  $g_q$  above stand for

$$\begin{aligned} f_q &= \frac{1 + 6x + 6x^2}{g_q + 12x^2 + 18x^3 + 18x^4}, \\ f_{\nabla E} &= \frac{g_q}{g_q + 12x^2 + 18x^3 + 18x^4}, \\ g_q &= 1 + 6x + 24x^2 + 54x^3 + 54x^4. \end{aligned} \quad (12)$$

Eq.<sup>1</sup> (23) for the reaction field gradient is valid but with the new  $f_q$ -factor above.

**Cavity field and cavity field gradient.** The solution to the problem for a cavity in a quadrupolar continuum polarized by an external field  $\mathbf{E}_0$ , with the new boundary condition (6), also changes compared to Eqs.<sup>1</sup> (26)–(30). The potential  $\phi_E$  at  $r > R_{\text{cav}}$  is

$$\phi_E = -\mathbf{E} \cdot \mathbf{r} + \frac{\mathbf{p}_{\text{ext},E} \cdot \mathbf{r}}{4\pi\epsilon r^3} \left( 1 - \frac{9}{g_p} \frac{L_Q^2}{R_{\text{cav}}^2} \frac{r + L_Q}{R_{\text{cav}}} e^{-\frac{r-R_{\text{cav}}}{L_Q}} \right). \quad (13)$$

The cavity field  $\mathbf{E}_{\text{cav}}$  is proportional to the external field  $\mathbf{E}_0$ , formally with the same  $Y_E$  coefficient, Eq.<sup>1</sup> (28), but with the new quadrupolar factors (9). The vector  $\mathbf{p}_{\text{ext},E}$  in Eq. (13) is the excess dipole moment of the cavity induced by the external field, and instead by Eq.<sup>1</sup> (29), it is given by

$$\mathbf{p}_{\text{ext},E} = -\frac{4\pi}{3} R_{\text{cav}}^3 Y_E (\epsilon - \epsilon_0) \mathbf{E}_0. \quad (14)$$

Finally, let us summarize the solution to the problem for a cavity in a quadrupolar medium placed in an external electric field gradient  $(\nabla \mathbf{E})_0$ . The cavity field gradient  $(\nabla \mathbf{E})_{\text{cav}}$  is proportional to  $(\nabla \mathbf{E})_0$  with the  $Y_{\nabla E}$  coefficient from Eq.<sup>1</sup> (33). The potential outside the cavity is

$$\begin{aligned} \phi_{\nabla E} &= -\frac{1}{2} \mathbf{r} \cdot (\nabla \mathbf{E})_0 \cdot \mathbf{r} + \frac{3\mathbf{r} \cdot \mathbf{q}_{\text{ext},\nabla E} \cdot \mathbf{r}}{8\pi\epsilon r^5} \\ &\times \left( 1 - \frac{18}{G_q} \frac{L_Q^2}{R_{\text{cav}}^2} \frac{r^2 + 3L_Q r + 3L_Q^2}{R_{\text{cav}}^2} e^{-\frac{r-R_{\text{cav}}}{L_Q}} \right). \end{aligned} \quad (15)$$

The excess quadrupole moment  $\mathbf{q}_{\text{ext},\nabla E}$  of the sphere induced by the external gradient  $(\nabla \mathbf{E})_0$  is given by the equation

$$\mathbf{q}_{\text{ext},\nabla E} = -\frac{8\pi}{15} R_{\text{cav}}^5 Y_{\nabla E} A_{\nabla E} \nabla \mathbf{E}_0. \quad (16)$$

The quadrupolar factors in these formulae are given by Eq. (12) and the expressions

$$\begin{aligned} g_{\nabla E} &= 1 + 9x + 39x^2 + 90x^3 + 90x^4, \\ A_{\nabla E} &= \left( 1 + 9x^2 \frac{g_{\nabla E}}{2g_q} \right) \epsilon - \left( 1 - 3x^2 \frac{1 + 3x + 3x^2}{g_q} \right) \epsilon_0, \\ G_q &= \frac{12g_q A_{\nabla E}}{15(1 + 6x^2)\epsilon - 10\epsilon_0}. \end{aligned} \quad (17)$$

**Reciprocal relationships.** Onsager<sup>9</sup> observed that the following reciprocal relation holds for the cavity field and the external dipole in a dipolar medium:  $\mathbf{E}_{\text{cav}}/\mathbf{E}_0 = \mathbf{p}_{\text{ext}}/\mathbf{p} = 3\epsilon/(2\epsilon + \epsilon_0)$  (his Eq. (11)). An important outcome from the revised boundary condition (6) is that such a relation is valid also in a quadrupolar medium

$$\frac{\mathbf{p}_{\text{ext}}}{\mathbf{p}} = \frac{\mathbf{E}_{\text{cav}}}{\mathbf{E}_0} = Y_E. \quad (18)$$

Analogous reciprocal relationship occurs for the external quadrupole and the cavity field gradient

$$\frac{\mathbf{q}_{\text{ext}}}{\mathbf{q}} = \frac{(\nabla \mathbf{E})_{\text{cav}}}{(\nabla \mathbf{E})_0} = Y_{\nabla E}. \quad (19)$$

The old boundary condition (2) leads<sup>1</sup> to results that disagree with Eqs. (18) and (19).

**The macroscopic polarizability and quadrupolarizability.** The macroscopic polarizability and quadrupolarizability of the medium are obtained in the manner described in Ref. 1. The result for the polarizability  $\alpha_P$  reads

$$\alpha_P \equiv \epsilon - \epsilon_0 = \frac{Y_E}{1 - \alpha_P X_p} \left( \alpha_p + \frac{1}{1 - \alpha_P X_p} \frac{p_0^2}{3k_B T} \right) C. \quad (20)$$

This is the sought generalization of Onsager's<sup>9</sup> formula for  $\epsilon$  to a quadrupolar medium. The respective equation for the macroscopic quadrupolarizability  $\alpha_Q$  of an Onsager fluid is

$$\alpha_Q \equiv 3\epsilon L_Q^2 = \frac{Y_{\nabla E}}{1 - \alpha_Q X_q} \left( \alpha_q + \frac{1}{1 - \alpha_Q X_q} \frac{\mathbf{q}_0 : \mathbf{q}_0}{10k_B T} \right) C. \quad (21)$$

Here, the factors  $X_p$  and  $X_q$  are given by Eqs.<sup>1</sup> (15) and (22), and  $Y_E$  and  $Y_{\nabla E}$  are given by Eqs.<sup>1</sup> (28) and (33)—but with the new expressions for  $f_p$ ,  $f_q$ ,  $f_E$ , and  $f_{\nabla E}$ , Eqs. (9) and (12). Eqs. (20) and (21) are setting the correct Onsager model for a quadrupolar liquid, instead of Eqs.<sup>1</sup> (50) and (53). The change is significant enough to affect most of the results presented in Ref. 1. Qualitatively, the results are similar, with one exception: according to Eqs.<sup>1</sup> (51) and (52), the quadrupoles have a stronger effect on  $\epsilon$  in the case where  $p_0 = 0$ , i.e., non-polar liquids; according to Eq. (20), the relative effect is not so different for polar and non-polar fluids. Quantitatively, in most cases, the new term  $\nabla^S \cdot \mathbf{D}^S$  in Eq. (6) leads to a significant change of the final values of  $\alpha_Q$  (up to 20%) and cannot be neglected. Correspondingly, Table<sup>1</sup> I and most figures in Ref. 1 are inaccurate—the revised ones follow.

**Results.** As in the previous work,<sup>1</sup> we used the following empirical relationship between the cavity radius and the density of the fluid:

$$\frac{m}{\frac{4}{3}\pi R_{\text{cav}}^3} = k_p \rho + k_0, \quad (22)$$

TABLE I. Values of the molecular multipole moments and polarizabilities, and the coefficients in dependence (22) of  $R_{\text{cav}}$  on  $\rho$ .

	Dipole moment $p_0$ (C·m) $\times 10^{30}$	Polarizability $\alpha_p/4\pi\epsilon_0$ ( $\text{\AA}^3$ )	Quadrupole moment $(q_0:q_0)^{1/2}$ (C·m <sup>2</sup> ) $\times 10^{40}$	Quadrupolarizability $\alpha_q/4\pi\epsilon_0$ ( $\text{\AA}^5$ )	$k_0$ (kg/m <sup>3</sup> ) in Eq. (22)	$k_\rho$ in Eq. (22)	$\text{dev}_\epsilon/\epsilon_0$ of Eq. (22) vs. the data for $\epsilon$
Ar	0	1.639	0	0.454	655.5	0.3134	0.0009
Kr	0	2.488	0	0.913	...	...	...
Xe	0	4.105	0	1.936	...	...	...
CH <sub>4</sub>	0	2.597	0	1.681	122.84	0.7019	0.0004
N <sub>2</sub>	0	1.737	4.08	1.12	342.2	0.5445	0.0005
CO <sub>2</sub>	0	2.98	11.43	2.21	235.64	0.9102	0.0009
CS <sub>2</sub>	0	8.215	8.88	11.40	721.2	0.5513	0.0017
C <sub>6</sub> H <sub>6</sub>	0	10.25	24.87	18.42	695.2	0.3300	0.0019
H <sub>2</sub> O	6.204	1.470	8.073	0.496	Eq. (23)		0.19
CH <sub>3</sub> OH	5.638	3.32	16.436	3.121	1991.3	0.3534	0.7

where  $m$  is the molecular mass. The values of the coefficients  $k_\rho$  and  $k_0$  we determined previously in Table I are based on the old defective variant of the Onsager model. The correct  $k_\rho$  and  $k_0$  are given in Table I here; they were determined by regression over the experimental data for  $\epsilon$  vs. the theoretical permittivity following from our new Eqs. (20)–(22) (solved for the unknown  $R_{\text{cav}}$ ,  $L_Q$ , and  $\epsilon$ ). In all cases but water, the analysis of the data for  $\epsilon$  suggested that  $R_{\text{cav}}$  is a function of  $\rho$  only. For water, as in Ref. 1, statistically significant temperature dependence was evident, and therefore, instead of Eq. (22) we used

$$\frac{m}{\frac{4}{3}\pi R_{\text{cav}}^3} = k_\rho \rho - k_T T + k_0. \quad (23)$$

For H<sub>2</sub>O, we compared the theoretical permittivities that follow from Eqs. (20)–(23) with the data points for  $\epsilon$ ; the dispersion was minimized with respect to the parameters of Eq. (23), leading to best values  $k_0 = 2853.7 \text{ kg/m}^3$ ,  $k_\rho = 0.1195$ , and  $k_T = 1.057 \text{ kg/m}^3 \text{ K}$  (slightly different from those determined in Ref. 1). The details for the experimental data and the values of the molecular parameters used in this Comment are described in Ref. 1.

Figs. 1–5 in Ref. 1 are inaccurate, due to the defective Eqs. 1 (50) and (53). Figs. 1–5 here show the correct results. For non-polar and non-quadrupolar fluids (Ar, Kr, Xe, CH<sub>4</sub>), the change is very small, so the respective Figs. 3 and 4 do not require a correction. For quadrupolar but non-polar molecules (N<sub>2</sub>, CO<sub>2</sub>, CS<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>), the values of  $L_Q$  calculated here at

the highest experimental densities are about 10% smaller than those in Ref. 1 (corresponding to an error in  $\alpha_Q$  of about 20%). In Fig. 3, the correct quadrupolar lengths of benzene calculated via Eqs. (20) and (21) are compared with those from Ref. 1, to highlight the importance of the term  $\nabla^S \cdot \mathbf{D}^S$  in Eq. (6). For polar species (H<sub>2</sub>O, CH<sub>3</sub>OH), the new values of  $L_Q$  are at most 5% smaller than those in Ref. 1 (corresponding to  $\alpha_Q$  by 10% smaller). The change in the values of  $R_{\text{cav}}$  compared to those in Ref. 1 is relatively small (e.g., 1%–2%) yet significant in view of the strong dependence of all properties of the quadrupolar liquid on  $R_{\text{cav}}$ .

The value of the dipole moment  $\mathbf{p}$  of a water molecule in liquid environment is larger than the intrinsic dipole  $\mathbf{p}_0$  of a molecule in the gas phase by a factor of  $1/(1 - \alpha_p X_p) = 2.17$  (which differs from the value 2.07 calculated previously<sup>1</sup> due to the different  $f_p$  factor in the expression for  $X_p$ ). The quadrupole moment of water increases by a factor of  $\mathbf{q}/\mathbf{q}_0 = 1/(1 - \alpha_q X_q) = 1.39$  (instead of<sup>1</sup> 1.36). This suggests that one of the approximations of the Onsager model—for the negligible molecular hyperpolarizabilities—fails even worse for the revised model of Onsager.

An important feature of the quadrupolar Onsager model is that it leads to a much smaller field intensity  $\mathbf{E}$  near the cavity compared to the original model: in the range  $r = R_{\text{cav}} \dots 3R_{\text{cav}}$ , using the results for the parameters of water at room temperature, one can obtain that the maximal value of  $E_r$  varies in the range  $3 \times 10^8 \dots 3 \times 10^7 \text{ V/m}$  (2 orders of magnitude smaller than the range obtained previously,<sup>1</sup> due to another arithmetic

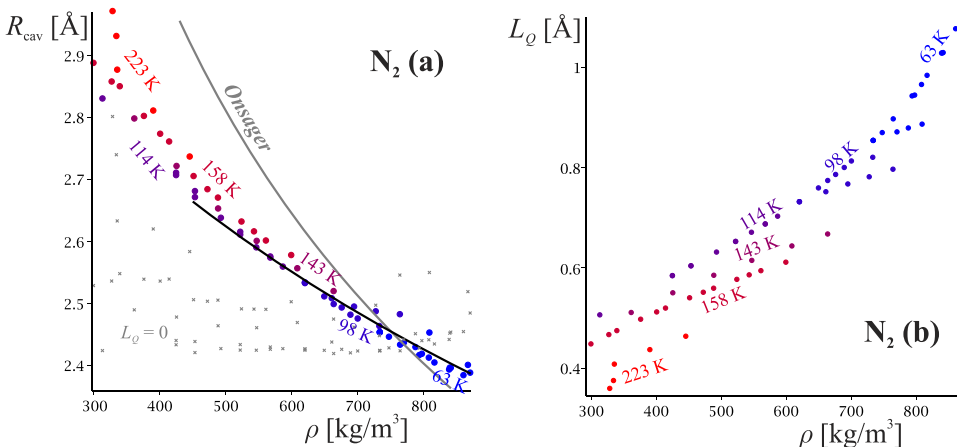


FIG. 1. (a) Cavity radius of N<sub>2</sub> calculated from Eqs. (20) and (21) and experimental data for  $\epsilon$  and  $\rho$ . The colour indicates the temperature. The gray symbols are Böttcher's  $R_{\text{cav}}$  following from the original theory of Onsager (Eq. (20) with  $L_Q = 0$ ). The black line is Eq. (22) with  $k_\rho = 0.545$  and  $k_0 = 342 \text{ kg/m}^3$ . (b) The quadrupolar length  $L_Q$  following from the same model and data. See Ref. 1 for details.

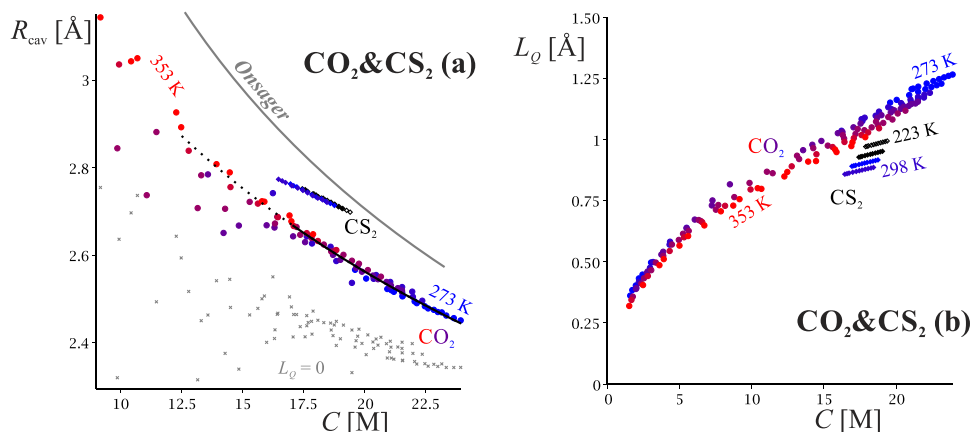


FIG. 2. (a) Cavity radius of  $\text{CO}_2$  and  $\text{CS}_2$  as a function of their concentration  $C$ , calculated with Eqs. (20) and (21) from experimental data for  $\epsilon$  and  $\rho$ . The colour indicates the temperature. The gray symbols are Böttcher's  $R_{\text{cav}}$  following from Onsager's original equation (Eq. (20) with  $L_Q = 0$ ). Gray line is Eq. (22) with  $k_\rho = 1$  and  $k_0 = 0$ ; black line is Eq. (22) with  $k_\rho = 0.910$  and  $k_0 = 236 \text{ kg/m}^3$  for  $\text{CO}_2$ . (b) The quadrupolar length  $L_Q$  following from the same model. See Ref. 1 for details.

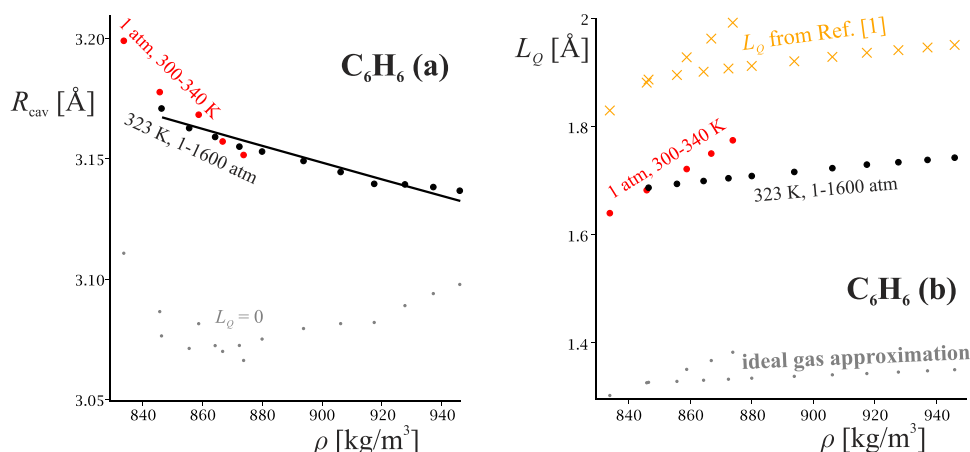


FIG. 3. (a) Cavity radius of benzene as a function of  $\rho$ , calculated with Eqs. (20) and (21) and experimental data for  $\epsilon$  and  $\rho$ . The red circles correspond to various temperatures (300-340 K) and pressure 1 atm, and the black ones—various pressures (1-1600 atm) and temperature 323 K. The gray symbols are Böttcher's  $R_{\text{cav}}$  following from Onsager's equation (Eq. (20) with  $L_Q = 0$ ). The black line is Eq. (22) with  $k_\rho = 0.330$  and  $k_0 = 695 \text{ kg/m}^3$ . (b) The quadrupolar length  $L_Q$  following from the same model (circles). Gray dots:  $\alpha_Q$  of an ideal gas. Crosses:  $L_Q$  calculated<sup>1</sup> with the wrong boundary condition 1. See Ref. 1 for details.

error). This field is still high and dielectric saturation can still be expected, but not as massive as estimated in Ref. 1. The dipole moment per each water molecule in the first coordination shell that follows from the Onsager cavity model can be estimated to be of the order of  $0.5 \times p_0$ . For comparison, the original model<sup>9</sup> of Onsager (with  $L_Q = 0$ ) predicts significantly higher field (up to  $8 \times 10^8 \text{ V/m}$  at  $r = R_{\text{cav}}$ ).

The comparison of the values of the macroscopic quadrupolarizabilities determined by Jeon and Kim<sup>11</sup> from Stokes shift data of coumarin in  $\text{CO}_2$  and  $\text{C}_6\text{H}_6$  ( $\alpha_Q = 0.42 \times 10^{-30} \text{ Fm}$  at  $\rho = 800 \text{ kg/m}^3$  for  $\text{CO}_2$  and  $2.6 \times 10^{-30} \text{ Fm}$  for  $\text{C}_6\text{H}_6$ ) with those following from the revised Onsager model

under the same conditions ( $\alpha_Q = 0.46 \times 10^{-30} \text{ Fm}$  for  $\text{CO}_2$  and  $1.9 \times 10^{-30} \text{ Fm}$  for  $\text{C}_6\text{H}_6$ ) shows good agreement for  $\text{CO}_2$  and acceptable for  $\text{C}_6\text{H}_6$ . The coincidence might be accidental since the Stokes shift formula of Jeon and Kim is based on a set of boundary conditions different from ours.<sup>1</sup> The calculated quadrupole length of methanol varies in the range  $L_Q = 0.79\text{--}0.82 \text{ Å}$ , Fig. 5, in satisfactory agreement with the value obtained from the data for the activity coefficient of NaBr in methanol solution,<sup>6</sup>  $L_Q = 1.1 \pm 0.2 \text{ Å}$ . The difference is most probably due to the neglected hyperpolarizabilities: according to the revised Onsager model, the dipole moment  $p$  of methanol is higher than  $p_0$  by a factor of 2.39 (compared to the

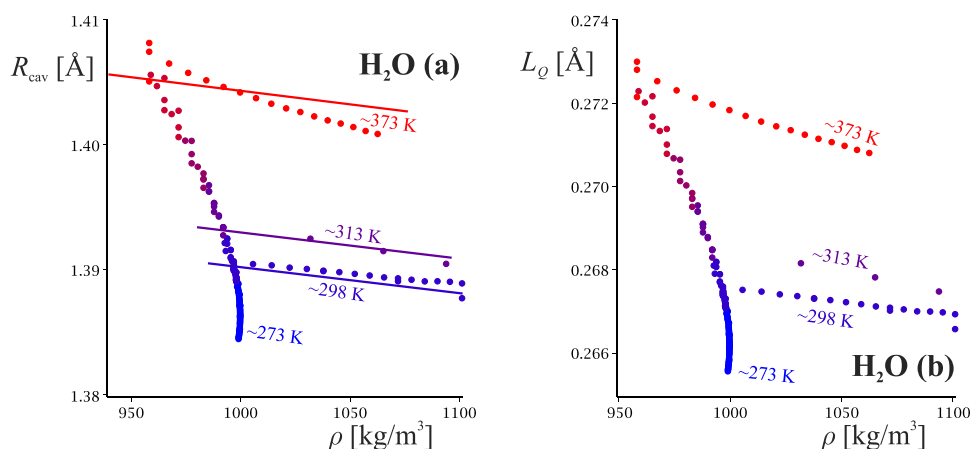


FIG. 4. (a) Cavity radius of  $\text{H}_2\text{O}$  calculated with Eqs. (20) and (21) and experimental data for  $\epsilon$  and  $\rho$ . The colour indicates the temperature. The lines are Eq. (23) at the indicated temperatures. (b) The quadrupolar length  $L_Q$  following from the same model. See Ref. 1 for details.



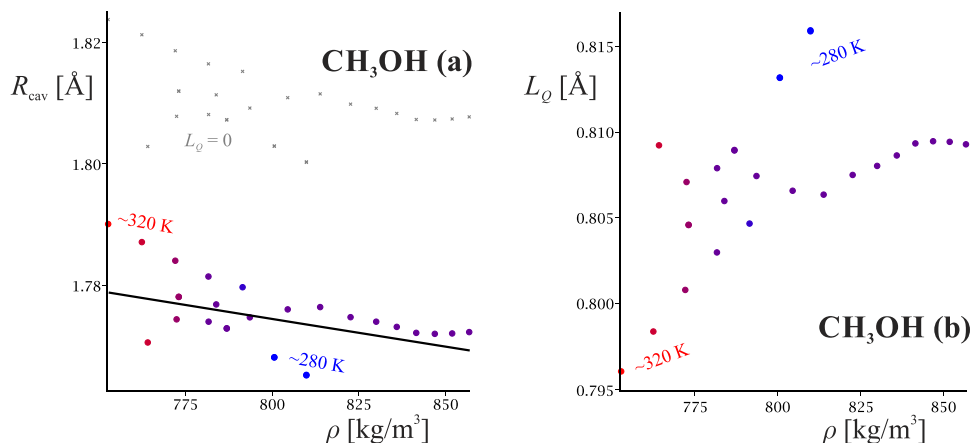


FIG. 5. (a) Cavity radius of methanol calculated from Eqs. (20) and (21) and experimental data for static permittivity and density. The colour indicates the temperature. The black line is Eq. (22) with the coefficients from Table I. The gray symbols are Böttcher's radii (obtained from Eq. (20) with  $L_Q = 0$ ). (b) The quadrupolar length  $L_Q$  following from the same model. See Ref. 1 for details.

previous<sup>1</sup> value 2.16), which is too high, and the reaction field is of magnitude  $2 \times 10^{10}$  V/m, large enough for the hyperpolarizabilities to play a role. Another problem with methanol is that its molecule is not spherical, cf. the discussion in Ref. 1.

**Clausius-Mossotti-Debye fluid.** We would like to use this document to answer a question that we have been asked on several occasions regarding the quadrupolarizability of a liquid, namely, what would a Clausius-Mossotti-Debye-like model give for the properties of a quadrupolar fluid? This model<sup>10</sup> assumes that the local field  $E_{\text{loc}}$  acting on a molecule in the cavity in the liquid is the sum of the external field  $E_0$  plus the field  $E_P = P/3\epsilon_0$  of a homogeneously polarized medium of polarization  $P$  outside the cavity (in contrast, in Onsager's model, the polarization is a function of the coordinates). A similar approach can be applied to a cavity in a homogeneously quadrupolarized medium of constant  $Q$ . However, it is easy to show that the potential inside such a cavity is constant, and therefore, the respective electric field gradient  $(\nabla E)_Q$  produced by the medium is zero. Consequently, the local electric field gradient is equal to the outer one, i.e.,  $(\nabla E)_{\text{loc}} = (\nabla E)_0$  (compared to the relation Eq. 1

(43) in an Onsager fluid). Therefore, the quadrupolarizability of a Clausius-Mossotti-Debye liquid is precisely equal to the quadrupolarizability of an ideal gas, Eq. 1 (1).

See [supplementary material](#) for (A) some of the derivations and (B) a sample Maple code for solving Eqs. (20) and (21).

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